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THE EFFECTS OF CARBON MONOXIDE ON THE ADSORPTION OF NITRIC OXIDE ON POLYCRYSTALLINE PLATINUM

Youn Seok PARK, Wha Young LEE*, Hyun-ku Rhee*,
Buick Pajung Sung* and Ho-In Lee**

Department of Chemical Technology, College of Engineering, Seoul National University, Seoul 151, Korea
*Department of Chemical Engineering, College of Engineering, Seoul National University, Seoul 151, Korea

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Abstract—The effects of carbon monoxide on the adsorption and desorption of nitric oxide on the surface of polycrystalline platinum foil have been studied using the technique of thermal desorption spectroscopy (TDS) under ultra-high vacuum conditions. It is suggested that the surface of polycrystalline platinum used in this study consists of Pt(111) plane, Pt(100) plane, and a small amount of high index surfaces. The α-CO pre-adsorbed at 300 K prevents indirectly nitric oxide from adsorbing on the sites of the surface giving α-No peak. The repulsive force between α-CO and α-NO is very strong, but a small amount of α-NO adsorbs even on the surface of platinum saturated by 50 L CO. The adsorption sites for β-CO coincide with those for β-NO, and predosing with more than 10 L CO blocks entirely the adsorption sites for β-NO. β-NO reacts readily with CO producing carbon dioxide and molecular nitrogen, and the reaction between CO and NO proceeds via Langmuir-Hinshelwood mechanism.

INTROUDCTION

The problems on environmental pollution formed by automobile exhaust gas are becoming more serious for the high increase in number of automobiles. The pollutants from automobile exhaust gas are mainly NO and CO [1]. Catalytic reduction of NO to molecular nitrogen and oxidation of CO to carbon dioxide are two important reactions in pollution control schemes. In order to develop a detailed understanding of these reactions, a number of basic researches are being performed [2,3]. Particularly, the studies using recent analytical instruments under ultra-high vacuum conditions are becoming more important [4]. It has been reported that the catalyst containing platinum group metals is highly active for this kind of oxidation-reduction reactions [5,6].

To elucidate adsorbing states of gas molecules on the surface of catalyst under ultra-high vacuum conditions provides catalyst-designers with many useful informations. NO, one of two main pollutants in automobile exhaust gas, has been studied less than CO. And the chemisorption of NO on metal surfaces is of considerable interest for the following reasons: First, NO has an unpaired electron in the antibonding $2\pi^*$ orbital. NO can, therefore, either donate or accept electrons in establishing a chemical bond. Second, the dissociation energy of NO is lower than that of N_2 or CO [7]. NO has been frequently used in the studies to clarify dissociation kinetics which would give some important informations on the interaction between molecules and surface.

NO adsorbs on the surface of platinum in bridged or terminal type via bonding between N atom and surface. Generally, it is known that NO adsorbed on platinum is dissociated to N and O atom with increase of surface temperature, but there is wide difference depending on the states of surfaces [8]. Ibach and Lehwald[9] used a dimer model to interpret EELS experimental observations, assigning that at low coverage NO exists in adsorbed NO monomer and at high coverage in adsorbed $(NO)_2$ dimer. A multiple-adsorption-site model was proposed by Gorte and Gland [10], assigning that at low coverage NO adsorbs in bridged type and at high coverage in linearly bound terminal one. On the other hand, Dunn et al. [11] proposed a broken-chain model to interpret IRRAS experimental observations, assigning that NO molecules adsorbed on contiguous surface sites interact strongly through cross terms in the quadratic potential-energy function coupling the NO-stretching coordinates. It is suggested from many reported papers about NO chemisorption that under low pressure a multiple-adsorption-site model is powerful and under high pressure a broken-chain model. But no plausible theory is accepted yet. The activity for NO dissociation

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**To whom all correspondence should be addressed.

decreases with the following order; Pt(100), Pt(110), Pt(111) [12].

In this paper, we report results for NO chemisorption and CO effects on that on the surface of polycrystalline platinum. Flash desorption technique is mainly used in this study. ESCA and AES are employed for the confirmation of surface cleanliness.

EXPERIMENTAL

The apparatus has been described in detail elsewhere [13, 14]. Reactant gases were introduced to the system by two variable-leak valves after purification. NO was purified through dry ice-acetone trap and the other gases through liquid nitrogen trap. Platinum foil was cleaned by repeating a cycle of heating to 1300 K followed by cooling to normal temperature under 1×10^{-6} Torr O_2 until the peaks of contaminants were disap- trum obtained after surface cleaning. Typical AES characteristic peaks of platinum appear at the positions of 43, 64 and 1967 eV, but carbon AES peak at 272 eV does not appear. The adsorption temperature was 300 K and the heating rate was 50 K/sec. The platinum foil was heated resistively, and temperature was measured by a chromel-alumel thermocouple spotwelded to the center of sample.

RESULTS AND DISCUSSION

1. NO TDS Spectra

Figure 2 shows NO TDS spectra at various NO exposures. Until NO exposure comes to about 1 L, only two peacks (β,γ) appear. And at higher exposures more than about 1 L, the third peak (α) appears. With the increase of NO exposure, α-peak shifts from 405 K to 365 K and β-peak from 485 K to 470 K. But γ-peak position is constant as 580 K regardless of the amount of exposure. Comparing α-peak with the previous results of NO TDS spectra obtained by Ibach and Lehwald [9] and by Campbell et al. [15] on Pt(111) plane, we can reason that the sites giving α-peak have a similar nature with those on Pt(111) plane. Also, comparing β-peak with NO TDS results obtained by Gorte and Schmidt [16], it seems that the sites giving β-peak have a similar nature with those on Pt(100) plane. It is considered that γ-peak is formed by recombination between N atom and O atom adsorbed strongly on high index steps and/or kinks.

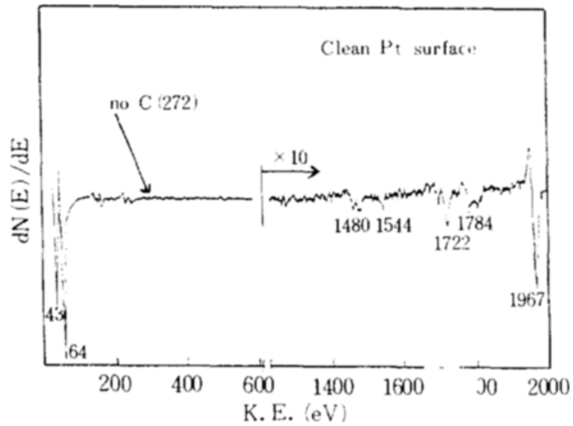

Fig. 1. AES spectrum obtained for a clean polycrystalline platinum surface.

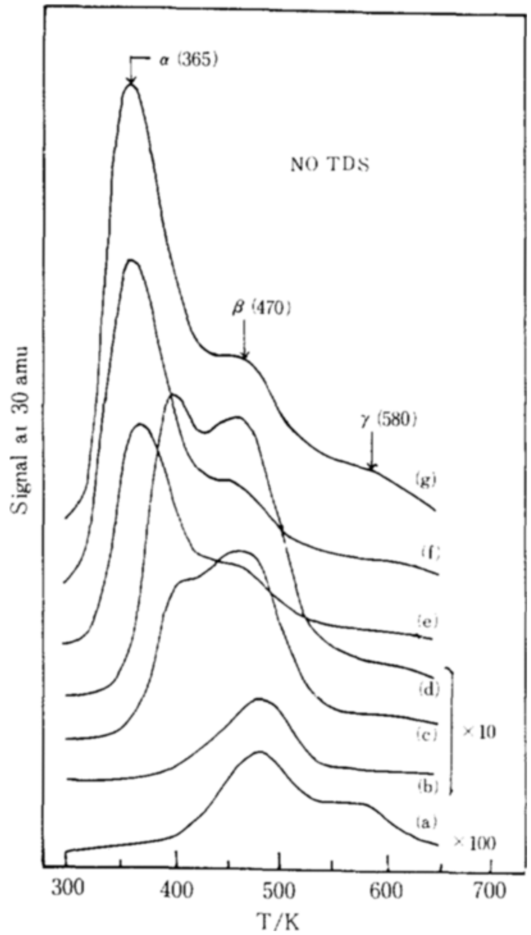

Fig. 2. Nitric oxide desorption spectra following exposures of the sample to; (a) 0.14 L, (b) 1 L, (c) 1.5 L, (d) 2 L, (e) 3 L, (f) 5 L, and (g) 10 L. For curves (a), (b), (c) and (d), the scales are increased as indicated.

Figure 3 shows N_2 TDS spectra obtained as mass number (m/e) 14 at various NO exposures. At higher exposures more than about 0.5 L, two peaks (α_1, α_2) ap-

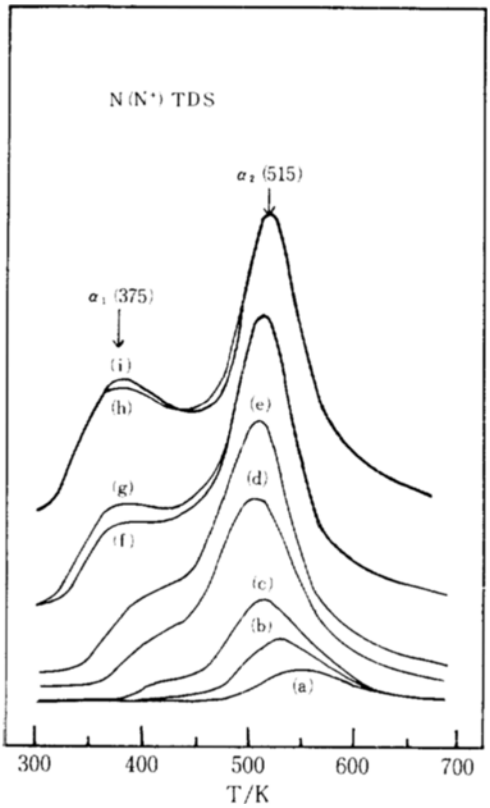

Fig. 3. Nitrogen desorption spectra following nitric oxide exposures of the sample to; (a) 0.1 L, (b) 0.5 L, (c) 1 L, (d) 2 L, (e) 3 L, (f) 5 L, (g) 8 L, (h) 10 L, and (i) 20 L.

pear. According to the TDS results reported by Gorte and Schmidt [16], NO desorbs dissociatively less than 2% on Pt(111) plane and more than 50% on Pt(100) plane. Because the positions of α_1 and α_2 peaks in Fig. 3 are quite similar to those of N_2 peaks obtained by NO dissociation on Pt(100), it is proposed that N_2 formation by NO dissociation is mainly due to the sites giving β-NO in Fig. 2. We can consider from the above two figures that the surface of polycrystalline platinum used in this study consists mostly of single crystal Pt(111), Pt(100), and a little steps and/or kinks.

Figure 4 shows NO, N_2, O_2 and CO_2 TDS spectra after 5 L NO exposure, respectively. The rate of CO_2 formation is maximum at the position of β-NO peak. We can conclude that CO_2 formation is caused mainly by β-NO, based on the following reasons: First, adsorbed oxygen atom and adsorbed CO react readily to form CO_2 on platinum at temperatures higher than 300 K and CO_2 does not adsorb in this range of temperatures [17]. The adsorbed CO is from the exposure to 6×10^{-9} Torr background CO for 50 sec. Second, the temperature

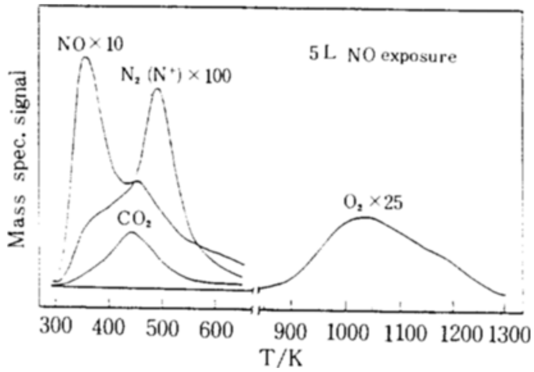

Fig. 4. Thermal desorption spectra for nitric oxide, oxygen, nitrogen and carbon dioxide after 5 L exposure of nitric oxide.

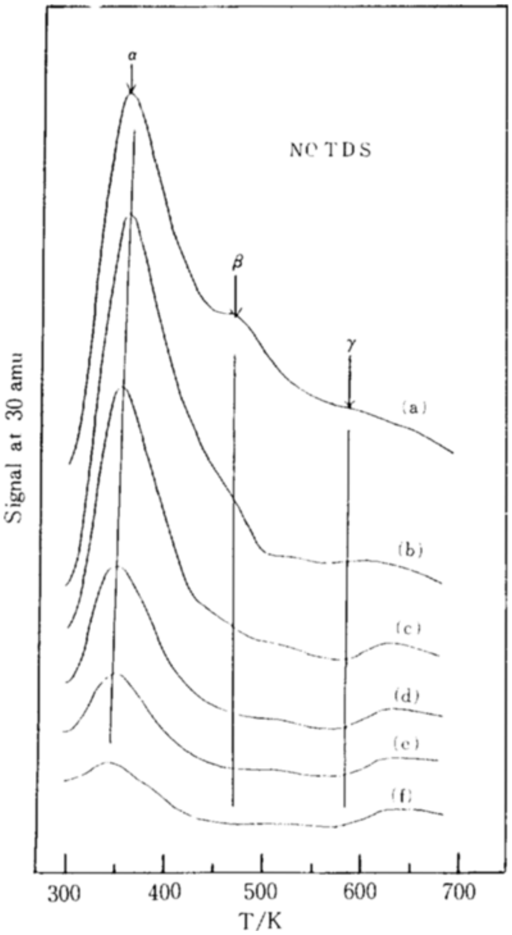

Fig. 5. Nitric oxide desorption spectra after 10 L NO exposure on the CO-preadsorbed sample. The amount of predosed CO is; (a) 0L, (b) 1L, (c) 5L, (d) 10L, (e) 20L, and (f) 50L.

where the rate of CO_2 formation is maximum is higher than α-NO peak temperature. The broad O_2 peak between 900 K and 1300 K is due to adsorbed oxygen atoms formed by NO dissociation. This peak position is identical with that by pure O_2 adsorption [18]. It is confirmed again by the results of Fig. 4 that α-NO and β-NO are caused by Pt(111) and Pt(100) surfaces, respectively.

2. Coadsorption of NO and CO

Figure 5 shows NO TDS spectra after 10 L NO exposure respectively on the sample pre-adsorbed with various CO exposures. The α-NO peak area is not influenced almost by 1 L CO pre-exposure, but decreases slowly with CO pre-exposure more than 1 L. And α-NO peak appears some what even on the surface of platinum saturated by 50 L CO exposure [13]. It is considered that the sites giving α-NO do not locate at the same positions as those giving α-CO, and that α-CO prevents α-NO from adsorption indirectly. The fact that the peak position of α-NO shifts from 365 K to 350 K with the increase of CO pre-exposure can be explained by strong repulsion between α-NO and α-CO. On the other hand, the area of β-NO is decreased suddenly by 1 L CO pre-exposure and β-and γ-NO are almost disappeared by about 10 and 1 L CO pre-exposures, respectively. The decrease of β-NO peak area arises from direct blocking of β-NO adsorption by β-CO and from CO_2 formation with adsorbed CO. And γ-NO reacts with adsorbed CO producing CO_2. It seems that the increase of NO partial pressure shown in the end of each curve results from NO desorption caused by heating of tantalum wires and feedthrus supporting the sample.

Figure 6 shows NO TDS spectra after 10 L NO exposure respectively followed by various CO exposures. In case of either CO pre-exposure or CO post-exposure, the effect of α-CO on α-NO is nearly identical. So, it is verified again that the sites giving α-NO are different from those giving α-CO and that these two kinds of sites locate very closely each other. The adsorption of β-NO is

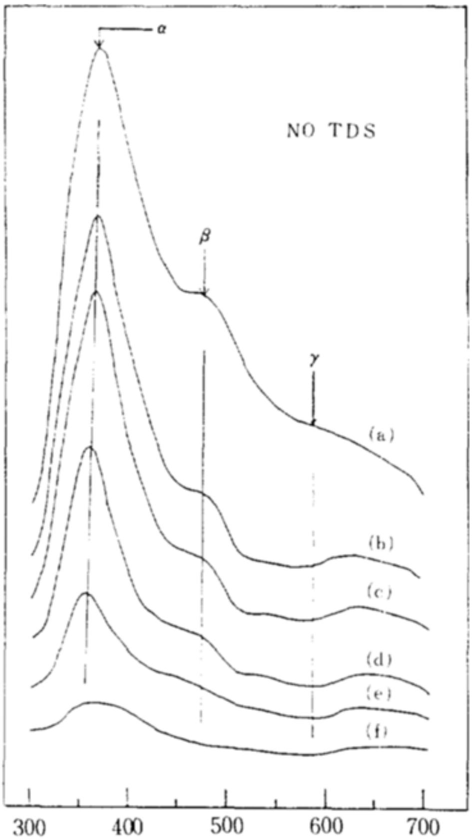

Fig. 6. Nitric oxide desorption spectra after 10 L NO exposure followed by CO exposure to; (a) 0 L, (b) 10 L, (c) 20 L, (d) 50 L, (e) 100 L, and (f) 300 L.

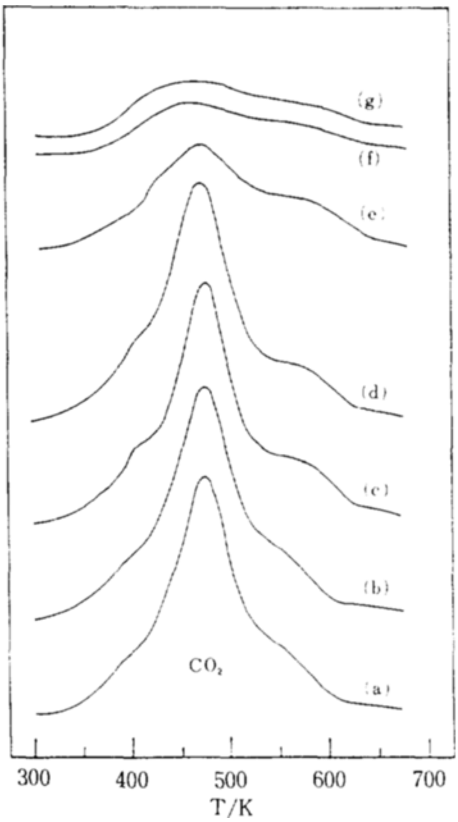

Fig. 7. Carbon dioxide desorption spectra after 5 L NO exposure on the CO-preadsorbed samples. The amount of predosed CO is; (a) 1L, (b) 2L, (c) 3L, (d) 4L, (e) 5L, (f) 10L, and (g) 20L.

less effected by CO post-exposure than by CO pre-exposure. It is considered that pre-adsorbed β-NO molecules occupy the sites of β-CO resulting in that the effects of β-CO become small. The peak area of β-NO decreases with much amount of CO post-exposure suggesting the displacement of β-NO by β-CO and the reaction of β-NO with β-CO. While, the peak area of α-NO decreases more rapidly than that of β-NO suggesting again that α-CO occupies different site from that for α-NO and that the two locate very closely each other. So, strong repulsion between pre-adsorbed NO and newly entered CO is expected resulting in desorption of NO. It is known that NO and CO are unreactive on Pt(111) up to the desorption temperature [19].

3. Interaction between NO and CO

Figure 7 shows CO_2 TDS spectra after 5 L NO exposure respectively on the sample predosed to various CO exposures. The temperature where the rate of CO_2 formation is maximum is 470 K, the β-NO peak temperature. Although the peak area of α-NO is larger than that of β-NO as shown in Fig. 2, the amount of CO_2 produced by β-NO is much more than that by α-NO. This fact suggests again that α-and β-NO are caused by Pt(111) and Pt(100), respectively. Adsorbed oxygen atom formed by NO dissociation reacts readily with adsorbed CO producing CO_2.

Figure 8 shows the plot of the total amount of CO_2 desorbed versus the amount of CO pre-exposure. The amount of CO_2 increases greatly with 1 L CO pre-exposure and shows a maximum in the range of 2-3 L CO pre-exposure, but decreases sharply with 4.5 L CO pre-exposure. Based on this, it is proposed that CO_2 formation from oxygen and carbon monoxide occurs via Langmuir-Hinshelwood mechanism in which the rate of CO_2 formations is maximum in case of two reactants existing with an appropriate ratio on the surface of catalyst.

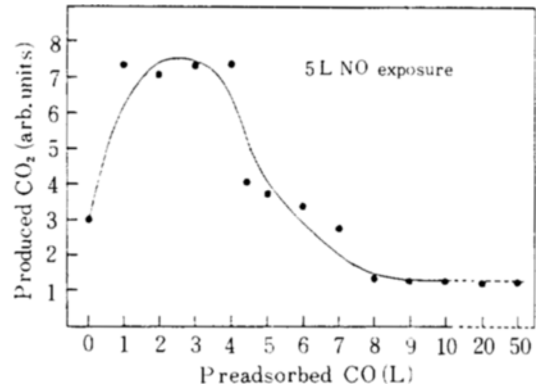

Fig. 8. Total carbon dioxide desorbed as a function of preadsorbed CO. The amount of NO exposure is 5L.

The amount of CO_2 at the first point for 0 L CO pre-exposure is due to background CO.

CONCLUSIONS

1. The surface of polycrystalline platinum used in this study consists mostly of Pt(111), Pt(100), and a small amount of high index steps.
2. The α-CO pre-adsorbed at 300 K prevents indirectly α-NO from adsorbing and the repulsive force between the two is very strong. A little amount of α-NO adsorbs on the surface platinum saturated by 50 L CO.
3. The sites giving β-NO coincide with those giving β-CO, and the adsorption of β-NO is entirely blocked on the surface predosed to more than 10 L CO.
4. β-No reacts readily with adsorbed CO producing CO_2 via Langmuir-Hinshelwood mechanism.

ACKNOWLEDGEMENT

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NOMENCLATURE

AES : Auger electron spectroscopy
EELS : electron energy loss spectroscopy
ESCA : electron spectroscopy for chemical analysis
IRRAS : infrared reflection absorption spectroscopy
K : kelvin(s) as a unit of absolute temperature
L : langmuir(s) as a unit of exposure
m/e : mass number, ratio of mass to charge in mass spectroscopy
Pt(100), Pt(110), Pt(111): Miller index for the considered surface of platinum single crystal
TDS : thermal desorption spectroscopy

REFERENCES

1. Anderson, J.R. and Boudart, M. (editors): "Catalysis," Vol. 5, Springer-Verlag, Tokyo (1984).
2. Lee, H. -I. and White, J.M.: *J. Catal.* **63,** 261 (1980).
3. Amirnazmi, A. and Boudart, M.: *J. Catal.* **39,** 383 (1975).
4. Czanderna, A.W. (editor): "Methods of Surface Analysis," Elsevier Scientific Publishing Co., Amsterdam (1975).
5. Hegedus, L.L. and Gumbleton, J.J.: *CHEMTECH.*, **10,** 630 (1982).
6. Acres, G.J.K.: *Chem. Ind.*, **22,** 305 (1974).

7. Pirung, G. Bonzel, H.P., Hospster, H. and Ibach, H.: *J. Chem. Phys.*, **71,** 593 (1979).
8. Gland, J.L.: *Surface Sci.*, **71,** 327 (1978).
9. Ibach, H. and Lehwald, S.: *Surface Sci.*, **76,** 1 (1978).
10. Gorte, R.J. and Gland, J.L.: *Surface Sci.*, **102,** 348 (1981).
11. Dunn, D.S., Severson, M.W., Golden, W.G. and Overend, J.: *J. Catal.*, **65,** 271 (1980).
12. Ivanov, V.P., Savchenko, V.I., Boreskov, G.K. and Taylor, K.C.: *Kinetics and Catalysis*, **69,** 163 (1978).
13. Park, Y.S., Lee, W.Y. and Lee, H.-I.: *Korean J. Chem. Eng.*, **2,** 75 (1985).
14. Park, Y.S. and Lee H.-I.: *J. KIChE.*, **23,** 79 (1985).
15. Campbell, C.T., Ertl, G. and Segner, J.: *Surface Sci.*, **115,** 309 (1982).
16. Gorte, R.J. and Schmidt, L.D.: *Surface Sci.*, **109,** 367 (1981).
17. Norton, P.R.: *Surface Sci.*, **44,** 624 (1974).
18. Nishiyama, Y. and Wise, H.: *J. Catal.*, **32,** 50 (1974).
19. Gorte, R.J. and Schmidt, L.D.: *Surface Sci.*, **111,** 260 (1981).